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**Title:** CHARACTERIZATION OF CONTAMINANT TRANSPORT  
USING NATURALLY OCCURRING U-SERIES DISEQUILIBRIA

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# **Characterization of Contaminant transport using Naturally-Occurring U-Series Disequilibria**

Mid Year Progress report  
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&

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## **Goals of Project:**

The main goal of the research is to understand the migratory behavior of radioactive contaminants in subsurface fractured systems by using naturally occurring U-series radionuclides as tracers under in-situ physico-chemical and hydrogeologic conditions. Naturally-occurring uranium- and thorium-series radioactive disequilibria can provide information on the rates of adsorption-desorption and transport of radioactive contaminants as well as on fluid transport and rock dissolution in a natural setting. This study will also provide an improved understanding of the hydrogeologic features of the site and their impact on the migration of radioactive contaminants. We intend to produce a realistic model of radionuclide migration in the Snake River Plain Aquifer beneath the INEEL by evaluating the retardation processes involved in the rock/water interaction. The major tasks are to (1) determine the natural distribution of U, Th, Pa and Ra isotopes in the groundwater as well as in rock minerals and sorbed phases, and (2) study rock/water interaction processes using U/Th series disequilibrium and a statistical analysis-based model code for the calculation of in-situ retardation factors of radionuclides and rock/water interaction time scales.

## **Technical Description of Work:**

In the decay series, elements such as U, Th, and Ra have several isotopes of different decay half-lives. This allows simultaneous solutions to the mass-balance model equations for all isotopes of an element, which in turn provides information on parameters such as residence time of fluid in the fractured rock, surface area and permeability, and dissolution rate of the rocks. By using decay-series disequilibria as a natural analog, the combined effects of variable speciation associated with formation of colloids and organic compounds are taken into account and the sorption capacity and retardation factors

determined by this approach are site-dependent. Because the decay series involves elements with a range of chemical properties, one may use the analog approach to simultaneously assess the migration of different radioactive wastes containing transuranic as well as alkali-, alkali earth, and lanthanide nuclides, in groundwater systems.

The proposed research will improve characterization of preferential flow and contaminant transport by providing the following scientific data:

1. Fluid residence time (transport rates) in the basalt aquifers at various locations. This information is useful for characterizing the preferential flow path or field in the fractured rock system.
2. The in-situ adsorption and desorption rate constants, as well as the retardation factors, of various radionuclide wastes. The retardation factor is fundamental to the characterization of contaminant transport since it describes the transport rate of radionuclides relative to that of fluids.
3. Rock dissolution rate and its relation to preferential flow and contaminant transport in the fractured rocks.

#### **Accomplishments to Date:**

To overcome unexpectedly low concentrations of some of the uranium-series nuclides in INEEL groundwater, we developed an in-situ filtration-enrichment sampling system in order to obtain groundwater samples sufficiently large to allow measurement of the short- and long-lived nuclides of the U and Th decay chains. This system has been used to successfully collect large-volume groundwater samples (~1000 liters) from 23 wells from the site. Radioisotopes of thorium ( $^{232}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{228}\text{Th}$ , and  $^{234}\text{Th}$ ), radium ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and  $^{224}\text{Ra}$ ), polonium ( $^{210}\text{Po}$ ), and lead ( $^{210}\text{Pb}$ ) were pre-concentrated in the field by passing the samples through two cartridge filtration units (connected in series at each well) containing  $\text{MnO}_2$ -impregnated acrylic fiber adsorbers. Small-volume samples were also collected for U and Ra concentration and U isotopic measurements by TIMS and for  $^{222}\text{Rn}$  by alpha scintillation counting. We have obtained a full suite of U- and Th-series nuclide measurements from a broad coverage of wells in the site.

On the basis of data collected thus far, we are able to arrive at some important conclusions for the INEEL site:

- Uranium concentrations range from 0.3 to 3.6 ppb and  $^{234}\text{U}/^{238}\text{U}$ -atomic ratios range between 0.000085 and 0.000168, corresponding to activity ratios of 1.6 to 3.1.
- Groundwater nearest the local recharge supplied by Birch Creek and Little Lost River has high  $^{234}\text{U}/^{238}\text{U}$  ratios, in contrast to the low to moderate values of groundwater dominated by the regional southwesterly flow of the Snake River Plain Aquifer.

Contours of high  $^{234}\text{U}/^{238}\text{U}$  ratios delineate preferential flow-paths extending southward from the Birch Creek and Little Lost River recharge areas. In these fast paths, isotopic modification due to mixing or water/rock interaction has been retarded due to fast groundwater flow. "Low-isotope ratio zones" separate preferential flow zones. These are interpreted to be due to greater extent of reaction with the host basalt.

- Activities of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{224}\text{Ra}$ , and  $^{234}\text{Th}$  range from 10 to 100 dpm/m<sup>3</sup> and those of  $^{210}\text{Po}$ , mostly from 1 to 10 dpm/m<sup>3</sup>, whereas the activities of  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ , and  $^{228}\text{Th}$  are generally less than 1 dpm/m<sup>3</sup>. Activities of Ra and Th are very low when compared to other groundwater systems indicating that the aquifer is an efficient scavenger of these elements.
- Systematic variations are found in activities of many decay-series nuclides. In general, the degree of disequilibrium among the U, Th and Ra isotopes decreases along flow pathways and away from local recharge drainages to the northwest of the site. The short half-lives of some of these nuclides (e.g.  $^{224}\text{Ra}$   $t_{1/2} = 3.66$  days) require that adsorption/ desorption must be important in controlling some of the isotope ratios. These trends delineate flow paths, which are consistent with those proposed on the basis of U isotopes.
- The observed U- and Th-series disequilibria enable quantification of the groundwater residence time, rock dissolution rates, and rates of sorption, desorption and precipitation (co-precipitation) of radionuclides in the groundwater. Groundwater residence times range from ~1 year in the northwest to ~100 years in central and southwestern parts of INEEL. Based on the residence time estimates, we successfully predicted the two preferential flow pathways delineated by  $^{234}\text{U}/^{238}\text{U}$  ratios. Rocks in contact with newly recharged groundwater in the northwestern part of INEEL dissolve at a rate of ~200 mg/L/y, whereas rocks in the southern part in contact with groundwater of ~100 years of age dissolve at ~50 mg/L/y. Modeled precipitation rates are hours to days for thorium, months for radium, and years for uranium.
- We have successfully estimated the degree of retardation due to rock-water interaction in the groundwater system at INEEL by modeling the observed radioactive disequilibria. Our model results indicate that adsorption of both radium and thorium by the aquifer solids at the site takes place on time scales of a few tenths to several seconds. The desorption times, on the other hand, are several days for radium and several years for thorium. Based on these sorption-desorption rate characteristics, we estimate that the in-situ retardation factors (i.e., the ratio of flow rate of fluid to those of dissolved radionuclides) are of the orders of  $10^6$  for  $^{230}\text{Th}$ ,  $10^4$  for  $^{226}\text{Ra}$ , and  $10^3$

for  $^{238}\text{U}$ . By analogy, we predict that the migration of lanthanide and alkaline earth fission products will also be heavily retarded.

- The model predicts that radionuclides sorbed on solids, which are exchangeable with the dissolved species through sorption/desorption, play an important role in affecting the decay-series disequilibrium in groundwater systems. The model also indicates that the major source of  $^{222}\text{Rn}$  in groundwater from the study area originates from decay of  $^{226}\text{Ra}$  sorbed on aquifer solid surface, rather than the previously held notion of direct alpha recoil from the solid  $^{226}\text{Ra}$  pool.

The retardation-factor estimates that we have derived contribute to our understanding of the disposal and migratory behavior of radioactive wastes at INEEL. These estimates allow us to delineate a rather large range of migration rates for possible contaminants in groundwater at the site and suggest that three groups of wastes can be identified in terms of their mobility. The migration of radionuclides with high ionic potential (readily hydrolyzed) such as thorium and lanthanide fission products is heavily retarded. The degree of retardation for alkali- and earth alkali- radionuclides (e.g.,  $^{133}\text{Ba}$ ,  $^{90}\text{Sr}$ , and  $^{137}\text{Cs}$ ) is such that these nuclides are unlikely to be transported far away from the contaminated areas. Uranium (and perhaps other transuranic radionuclides that occur in the +5 and +6 oxidation state) displays relatively high mobility in the aquifers we have studied.

Our results have clearly demonstrated that uranium-series disequilibrium, when used in a natural analog framework, can provide information that is difficult to obtain from laboratory experiments. Such information is critical for simulating the radionuclide transport in the far field. The conceptual model and major results for this project have been summarized in abstracts and three manuscripts to be submitted for publication. The following list shows presentations at national and international meetings completed under this sponsorship to date:

- Roback, Robert C., Murrell, Michael, Nunn, Andy, Johnson, Thomas, McLing Travis, Luo, Shangde and Ku, Richard, "Groundwater mixing, flow-paths and water/rock interaction at INEEL: Evidence from uranium isotopes," *Geological Society of America, Abstracts with Programs*, v. 29, no. 6., 1997.
- Luo, S., Ku, T. L., Roback, R., Murrell, M., and McLing, T., "Uranium-Series Disequilibria In Groundwater: Assessing Radionuclide Migration," *9th International Conference on Isotope Geology, Cosmochemistry and Geochronology*, Aug. 21-26, Beijing, 1998.
- Luo S., Ku T. L., Roback R., Murrell M., and McLing T., "Assessing in-situ radionuclide transport based on uranium-series disequilibrium in groundwater", Fall AGU Meeting, Dec. 6-10, 1998, San Francisco, *EOS Trans. Amer. Geophys. Un.* 79, F354, 1998.

Roback R. C., Murrell M. T., Nunn, A., Luo S., Ku T. L., and McLing T., "Uranium and thorium series isotopes in fractured rocks at the INEEL", Fall AGU Meeting, Dec. 6-10, 1998, San Francisco, *EOS Trans. Amer. Geophys. Un.* **79**, F343, 1998.

**Projections:**

The objectives of the project will be completed on schedule. Most of the analytical work has been completed. Initial modeling of the data has been complete. We are in the process of refining our models. Manuscripts have been prepared and are in the final stages of refinement prior to submission.

**Funding:**

Spending levels have been as projected for the LANL part of the project and we expect that funding will be sufficient to complete the project within budget.

**Issues/Problems:**

Problems encountered during the first year of the project were overcome. No new problems were encountered.

**Corrective Actions:**

NA

**Additional Information:**